Metal Phosphatizing Operations

Fact Sheet, Minnesota Technical Assistance Program, University of Minnesota

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Reducing Phosphorus Discharge and Water Use

When discharged into natural waterways, excess phosphorus results in nuisance algae blooms which reduce water transparency and decrease the oxygen available to aquatic animals.

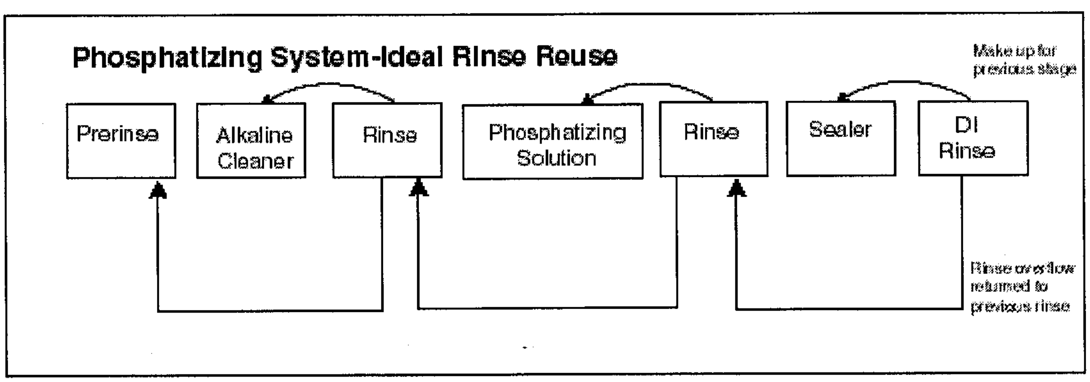
As the Minnesota Pollution Control Agency (MPCA) works to establish effluent phosphorus limits and phosphorus monitoring requirements for municipal treatment facilities, these facilities are looking to their industrial users to reduce phosphorus in their sewer discharge. Metal phosphatizing operations are a large industrial source of phosphorus in wastewater. When companies minimize phosphorus discharge from these operations they save by reducing chemical and water use.

Phosphatizing helps prevent corrosion and prepares the metal surface for improved paint adhesion. Less commonly, phosphatizing is used to improve the lubricity (slipperiness) of part surfaces. The phosphatizing process can vary widely. A spray wand is a simple one-stage cleaner/phosphatizer generally used on larger, low-volume products that do not require a high degree of corrosion resistance or adhesion. On the complex end are large, automated seven-stage conveyorized systems used for high volume component manufacturing and the highest surface property specifications. Three, five and six-stage systems are also common.

A typical system would start with alkaline cleaning then go through a rinse, phosphate coating, rinse and a seal rinse. For a medium-sized five-stage phosphatizing system, a five gallon-per-minute (gpm) rinse flow (600,000 gallons per year for one shift) is fairly typical. A greater flow rate may indicate an opportunity for decreasing water use.

Ideal Rinse Reuse

Most phosphatizing operations were built when water and wastewater disposal were not costly. Now these costs have risen and an ideal system should maximize rinse reuse to minimize chemical and water loss (see diagram below). Overflow from the rinses can be used as 1) make up for evaporation and dragout losses to the previous static chemical bath, and 2) a cascade rinse for the previous rinse stage.



Modify an existing system. The following changes would have the greatest benefits :

1. Look at reusing water where it will enhance the quality of cleaning. Reuse deionized (DI) water first to maximize the benefit of its purity and because of its cost (see Rochester Powder Coating , page 3).
2. Cascade the rinses where the overflow volumes are greatest (i.e., greater than five gpm). Cascading the phosphatizing rinse back to the cleaning rinse can cut rinse flow in half. Also, the acidic phosphate chemical that is returned with the rinse neutralizes the alkaline cleaning carryover that would otherwise degrade the phosphate chemistry. No new contaminants are introduced.
3. Heated tanks loose the most volume to evaporation. Use overflow from the subsequent stage as the make up.
4. Add a prerinse before the cleaner stage to wet soils. This helps loosen and remove soils. The cleaner is more effective and a significant amount of soils are kept out of the system. Reuse water by cascading overflow from the cleaning rinse to the prerinse.

Water and Chemical Use Reduction Tips

Bath concentrations. Maintain phosphate bath concentrations and chemical metering of wand applicators within the correct operating range, using the chemical supplier's recommendation. If a range is given, try operating at the low end. This may require greater care by the operators. Lower operating concentrations reduce the loading to the rinses, which can lead to reduced flow rates and phosphate losses to effluent. Also, monitor solution contaminant concentrations. This may be best and most easily done by installing conductivity meters which measure total dissolved solids (TDS).

Reduce carryover. Keep the chemistries in their tanks by reducing carryover. Design parts for drainage by avoiding blind holes and recesses while designing in drain holes where possible. Rack parts for good drainage. Angle parts so that the solution drains off one point—not an edge—of the part back into the bath.

Design the system with adequate drip time. For dip tank operations, hold parts above the tank to allow solution to drain back into the tank. Holding parts above the tank for 15 to 30 seconds returns 40 to 50 percent of the dragout back into the tank.

Modify drain boards between stages to drain back to the previous stage. Multistage spray systems should have drain zones between stages that provide for similar drain times—15 to 30 seconds minimum. Consider a fine, low-volume mist arc or spray rinse between stages to remove more carryover.

Use clean water. Consider using deionized (DI) or reverse osmosis (RO) water for making up chemical baths and possibly for rinses. DI water greatly decreases the dissolved solids present which in turn lengthens the bath life and reduces the volume of chemicals used and discharged. Also it reduces the volume of sludge generated by treatment of wastewaters.

Automated systems. Ensure all process controls are properly set (i.e., speed, chemical additions) and that they are periodically calibrated and maintained. Conductivity controls are particularly sensitive—consider using inductive conductivity sensors to reduce maintenance requirements. Quality parts are not an indicator of good system control. Poorly maintained control systems can create quality products by overusing water and chemicals. Frequency of bath turnover may be a better indicator.

Water flow. Measure and control water flow. Flow meters give a quick indicator of water overuse.

and the malfunctions that lead to overuse. Metering valves can be used with flow meters to control flow rates. In the absence of flow meters, use flow restrictors to control flow. Always avoid using ball valves in water lines unless a wide open flow is desired. Small changes in ball valve position can result in large changes in water flow rate. Although cheap, they are appropriate only as on/off valves.

Filter baths. Remove solids that could build up in the tank or clog nozzles. Skim oil off the alkaline cleaning tank.

Spray nozzles. Clean spray nozzles. Plugged nozzles cause some areas of the parts to be poorly cleaned or coated. A common response to quality failures is to increase flows and the frequency of bath changes. Often just cleaning the nozzles would ensure that the solution cleans the parts. Properly position nozzles for an ideal spray pattern that ensures the solution cleans the parts.

Procedures. Train employees on proper operation of the phosphatizing system. Conduct daily inspection. Look for tank leaks, valve leaks, evidence of controller malfunctions and plugged nozzles.

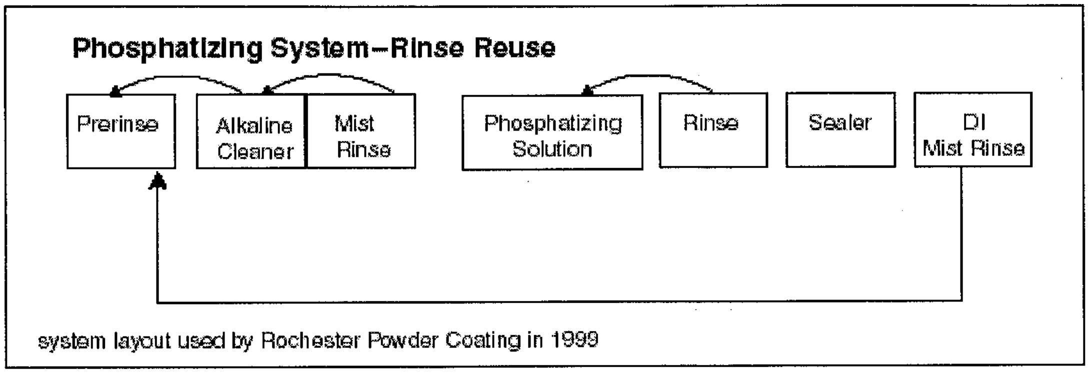
Rochester Powder Coating

Reducing Phosphorus Discharge-Success Story

Rochester Powder Coating (RPC), Rochester, Minnesota, is a job shop that paints sheet metal parts using powder coating. Prior to painting, the sheet metal goes through a phosphatizing line. By embracing pollution prevention practices, RPC reduced its phosphorus discharge by 98 percent over two years.

In October 1995, the discharge from the RPC phosphatizing system was 410 mg/L going into the City of Rochester's sewer system. With impending phosphorus limits, RPC and the City of Rochester began to look for ways to reduce this phosphorus discharge. RPC implemented an aggressive approach to maximize the use of phosphate instead of discharging it. First, RPC began to monitor solution content every two hours. This ensured that the concentration was within the proper operating range so that they weren't using too much or too little solution. They also added more-efficient spray nozzles to the phosphating risers which ensured that the solution reached the part and wasn't wasted.

In 1995, RPC installed a five-stage cleaning/phosphatizing system, which includes alkaline cleaner, rinse, phosphatizing, rinse and sealer with a partial rinse return to the phosphating bath. This prevented loss of phosphorus by returning it to the bath to work some more. Along with installing this system, RPC instituted rigorous monitoring, maintenance and worker training. In 1997, a sixth stage, deionized (DI) rinse, was added to enhance corrosion resistance and recycle phosphate cleaning solution back for reuse in the mist rinse just prior to phosphatizing. This provides cleaner parts going into phosphatizing. Although RPC has increased its production and increased discharge by 30 percent, phosphorus discharge concentrations have been lowered to 8 mg/L.



Federal-Mogul Corporation

Identifying Phosphorus Sources- Success Story

MnTAP funded a student intern at Federal Mogul, a manufacturer of diesel and compressor pistons and cylinder sleeves, to identify the sources of phosphorous in their manufacturing plant and to determine a strategy for reducing the quantity ending up in the wastewater. The two main sources of phosphorus were a phosphate coating process (96%) and plant maintenance cleaning chemicals (4%).

During the student's time at the company, all of the cleaning chemicals were switched over to non-phosphorus containing materials. The substitutes performed as well as or better than the conventional phosphorous containing materials.

Changes to the phosphating line were suggested. They included typical actions like dragout reduction by having a lag time in transfer to the next step, fog-like rinsing, counter current flow in tanks. Also, procedures were recommended for more routine and careful maintenance of the baths to minimize chemical use and disposal, and to ensure that the proper coating quality was achieved. Approximately 50 percent of the total phosphorus from the process could be reduced with the above changes.

Hoffman Engineering Company

Reducing Water Use-Success Story

Hoffman Engineering Company, a manufacturer of metal and composite enclosures in Anoka, reduced water use in a painting pretreatment process with the help of a MnTAP intern. Three of the four washer stages were modified to conserve water. These changes resulted in estimated savings of $32,000 and 3.5 million gallons of water annually. Savings from decreased chemical use was not calculated.

Primarily by installing flow meters, automated conductivity meters and control valves, Hoffman gained better control of their bath concentrations and rinses. These changes helped them identify leaks and malfunctions as well as decreased the loss of bath chemicals. Drain zones were also modified to return more solution to each respective preceding stage.

Phosporus Alternatives

Research for substitutes for phosphatizing compounds is ongoing. A few options are currently available. If improved paint adhesion to aluminum substrates is the goal, Sol-Gel processes[1] and abrasive blasting procedures[2] have been developed.

Also, there is a one-stage, no-rinse process for small to medium scale operations. It incorporates residual surface oils into the coating so excess solution can be captured and reused creating zero-effluent from the process[3].

Treating Phosphorus Discharge

Once phosphorus reduction efforts have been put in place, facilities may still need to lower the phosphorous concentrations in their wastewater. It can be lowered by precipitating phosphorous with ferric chloride, lime or alum. Ferric chloride is generally the most efficient precipitation agent. Treatment dosage will vary with local water chemistry and the phosphatizing chemicals used. However, a 20 mg/L ferric chloride dose and a 40 minute resident time in the settling tank are reasonable starting points in trying to reach a phosphorous concentration of less than 2 mg/L.

Regulations

Categorical discharge permits. If a facility does metal phosphatizing, it is subject to the U.S. Environmental Protection Agency's metal finishing standard that limits the concentration of seven metals, cyanide and total toxic organics (TTO) in waters that are sewered. Contact the MPCA's Water Quality Pretreatment Division at 651/296-6300 or 800/657-3864. Large municipal wastewater treatment facilities also deal with this regulation for industrial facilities in their areas.

Hazardous waste sludge. If wastewaters from aluminum phosphatizing operations are treated and a sludge is produced that sludge is a listed hazardous waste [F019] and must be managed as one.

More Information

MnTAP has a variety of technical assistance services available to help Minnesota companies reduce and manage their industrial waste. If you would like MnTAP assistance call 612/627- 4646 or 800/247-0015 from greater Minnesota.

Sources

1. Zheng, Haixing. *An Alternative to Anodization: Sol-Gel Solutions for Metal Finishing.* Metal Finishing, December 1998, 35.

2. Ault, Peter J. and Mike Starks. *Abrasive Blasting as an Alternative to Chromate Conversion Coating on 5086 Series Aluminum.* Metal Finishing, July 1999, 30-33.

3. Carpenter, Scott. *One-Step, Zero-Effluent Organic Phosphating.* Metal Finishing, September 1999, 56-60.

(10/99-64)

MnTAP main page

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Article Archives

Factors in Deciding Whether to Recycle Wastewater

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by: John Russo
Pages: 21; August, 1997

There are many factors involved in deciding to recycle wastewater, from increasing stringency of discharge regulations to a life cycle cost analysis. It is becoming typical that when all is considered, the question of why recycling wasn't considered sooner would be asked.

Recycling Methods

There are three general approaches:

o *Closed-loop*: Recycling all wastewater or chemical used, usually with ion exchange resin or membranes.

o *Zero-discharge*: Discharging no wastewater by using ion exchange, evaporation, and/or membranes.

o *Wastewater minimization*: Recycling most of the wastewater using membranes.

Which to consider depends upon a life cycle analysis and the potential for noncompliance or future disposal liability. Evaluating the following three factors will help you to focus on the critical areas of an investment.

Regulation Factors

o Limits on water usage for operations because of municipality restrictions

o Management time: record keeping and reporting of test results and inspections for regulatory agencies o Compliance for septic system discharge (ground water) is usually very expensive and you are indefinitely liable for contamination

o Future regulatory liability and cost to dispose of hazardous waste

o Fines for noncompliance with discharge regulations

o Laboratory testing of the wastewater being discharged

Economic Factors

Often, not all cost data is considered because individual factors are not very large. However, together they can easily outweigh the cost of recycling. Potential savings include the reduction or elimination of:

o Capital cost

o Water usage

o Wastewater discharge

o Chemical consumption (cleaners, coolants, etc.)

o Maintenance costs

o Operating costs

o Waste hauling

o Energy

o Oil (reuse as a heating fuel additive)

o Heavy metal (reuse of metal)

o Existing wastewater operations

Process Improvement Factors

It is common to increase effectiveness and efficiency of systems and operations:

o Less contamination of downstream processes

o Better water quality eliminates water spotting

o Reduction in the build-up of cleaner contaminants

o Better part surface quality for later operations

Mission Decision

The factor lists provide a starting point for a user to detail the pros and cons. For new process operations, selecting the best system requires that the entire cleaning process be considered simultaneously.

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Return to Cleaning Technology Profiles

Water treatment is necessary to reduce the level of contamination present in effluent water; therefore, it is a consideration when selecting and operating many cleaning systems.

Contaminants of concern may include insoluble oils, emulsified oils, other dissolved organics, suspended solids, and dissolved solids (eg, chlorides, nitrates, phosphates, and metals). Consult the Publicly Owned Treatment Works (POTW) regarding acceptable criteria for pH, biological oxygen demand (BOD), and chemical oxygen demand (COD). The requirements for discharge to the local POTW vary from state to state, municipality to municipality. Specific discharge criteria will be noted on your permit.

Pretreatment
Pretreatment may consist of a variety of unit operations, all performed to reduce the volume of solids and wastewater.

Filtration/screening is commonly used to remove any large particulate matter that should not enter the main treatment system.

Evaporation is used to reduce the volume of water needed for further treatment. The water is evaporated by heating it to its boiling point, or under vacuum. The contaminants then become concentrated within the remaining solution. The water is transferred to a holding tank, where it is allowed to cool to room temperature. Then, it is either discharged to the POTW (with the necessary permits and approvals in place), or moved along for further treatment.

Treatment Methods
pH
Wastewater operations can use pH control in order to promote solubility or flocculation of contaminants at various stages of treatment.

Solids
Acid conditions are commonly used to enhance break-up of the oil-water emulsion. Acids also make anions (eg, phosphates) react more readily with materials such as lime and ferrous oxide in order to make them separate. Once the "lock-up" reactions occur, the solution enters a "floccing" stage.

A cationic flocculant polymer is added at this stage. This aids both in the formation of filterable particulate and in the adsorbtion of oils and other organics to solids. An anionic coagulant can then be added to enhance particulate agglomeration, thus making it easier to filter.

The wastewater is pumped to a clarifier, where contaminated solids settle to the bottom of the chamber as sludge. The sludge is then dried via a filter chamber in preparation for disposal. The supernatant liquid is pumped to a process tank for pH adjustment and release back to the POTW.

Oils
Traditional mechanical separation of oil from wastewater involves the use of skimmers, tank-overflow, and decanting methods. These end-of-pipe (EOP) methods can be inefficient, increase maintenance downtime, create disposal problems, and increase costs.

Gravity separation of non-emulsified oils within wastewater can occur in the clarification tank. Optimized influent and effluent flow rates allow efficient separation of the lighter oil layer from the water. An inclined plate will direct the flow of the oil layer away from the wastewater. The oil droplets coalesce into larger globules and rise on the plate underside, while the sludge particles flow over the plate separator to the tank bottom.

A current method of oil-water separation uses Bernoulli's principle. The wastewater is split into two laminar flows. Oil is continuously collected and concentrated in a second chamber, which is separated by a baffle from the primary chamber and a reduced-pressure area below. The reduced pressure directs the flow of water down, away from the second chamber.

The oil is recovered from the top of the concentrated layer upon reaching a design thickness. Higher quality oil is recovered this way and then likely reused or burned as fuel.

Activated carbon
Activated carbon filters can remove organic constituents from the wastestream. An activated carbon filter is capable of absorbing material many times its own weight. The organic matter is absorbed within the extensive pore network of the carbon.

UV treatment
Ultraviolet (UV) light is an effective means to destroy organic chemicals and biological organisms. A UV-oxidation system can be employed, as necessary, to reduce the BOD of the wastewater.

Ion-exchange treatment
Ion exchange involves cationic and/or anionic species being adsorbed onto a resin. The ions will attach to the resin until the resin is saturated. The resin can then be regenerated by the manufacturer.

Selection Criteria and Compatibility Concerns
Each of the above unit operations may or may not be applicable to all water treatment systems. The requirements of a wastewater system are governed by the extent of contaminant reduction necessitated by POTW permit requirements. Below are criteria to be considered prior to installation of a wastewater system:

- Wastewater treatment options should be studied by an engineer to assess process alternatives. The system should be optimized for proper flow rates, filter capacities, throughputs, etc., for the contaminant reduction required by the discharge permit.
- Capital and operating costs may justify recycling of wastewater in a

closed-loop system. Capital costs of a closed-loop system vary depending on the system capacity and complexity. However, long-term profits may outweigh short-term capital expenses.

- Process chemistries must be thoroughly reviewed to determine impact on treatment process.
- Design, maintenance, and operations should have contingencies for downtime.
- Equipment configuration should be considered (wash tank, rinse tank, motorized equipment).
- Annual operating costs should be considered (utilities, materials, labor, maintenance, disposal costs).

Additional unit operations that can be included in a wastewater treatment system are microfiltration, ultrafiltration, and reverse osmosis. These are discussed in the technology brief for Recycling/Filtration Systems.

Find Out More!

For more information on wastewater treatment, see the following in Precision Cleaning Web's Article Archives:

Fundamentals of Aqueous Cleaning: Materials, Equipment, and Waste Treatment
by Charles Sexton; June, 1996

Aqueous Cleaning: The Basics & Beyond in a World of Emerging Needs
by Frank Cala; January, 1997

Managing Hard-to-Treat Wastewaters
by Robert J Masini; August, 1997

Factors in Deciding Whether to Recycle Wastewater
by John Russo; August, 1997

Optimizing Aqueous Cleaning Using Vortex Flow Filtration
by Gregory S Savage; March, 1998

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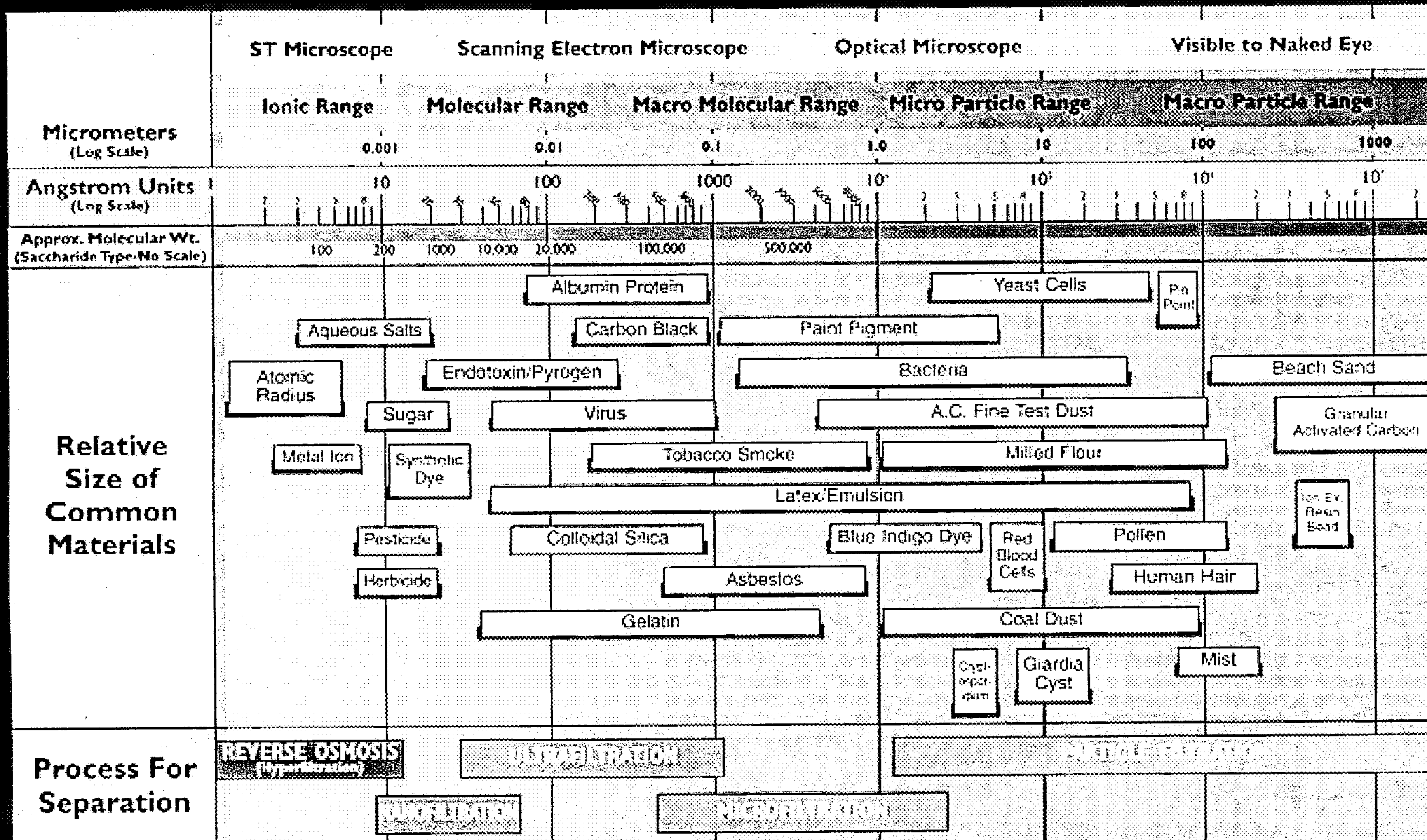
The Filtration Spectrum



Note: 1 Micron (1x10⁻⁶ Meters) ≈ 4x10⁻⁵ Inches (0.00004 Inches)
1 Angstrom Unit = 10⁻¹⁰ Meters = 10⁻⁴ Micrometers (Microns)

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Applicable Treatment Technologies for Wastewater Reuse

Treatment technology	Description	Applications	Limitations
Reverse osmosis	Uses the principles of osmosis and differences in pressure to separate dissolved salts in a solution from water by filtering the wastewater through a semi permeable membrane.	Removal of BOD, COD, TSS, NH, -N, TDS, and phosphorus	Cost Scaling pH and temperature sensitivity Pretreatment may be required Concentrate may require treatment or disposal
Electrodialysis	Electrodialysis concentrates or separates ionic species contained in a solution by passing the solution through semi permeable ion-selective membranes.	Removal of TDS and recovery of metal salts	Chemical precipitation on membrane Pretreatment may be required Cost
Ultrafiltration	Similar to reverse osmosis, ultrafiltration uses porous membranes to remove dissolved and colloidal materials from solutions; however, ultrafiltration operates at lower pressures and is generally limited to removing larger molecules.	Removal of TDS, turbidity, and oil	Cost Scaling pH and temperature sensitivity Pretreatment may be required
Ion exchange	Ion exchange removes specific ions from a solution by exchanging them with ions bound to a specifically formulated resin. The resin requires back washing and regeneration once its capacity has been reached.	Removal of TDS and toxic metal ions, and reduction of hardness by removing calcium and magnesium ions.	Spent resins and regenerants (i.e., acid, caustic, or brine) must be disposed High concentrations of suspended solids can reduce the efficiency of the resin
Activated carbon	The activated carbon process uses either granular or powdered carbon to treat wastewater by absorbing many organic and inorganic compounds. Once the capacity of the carbon has been reached, it must be regenerated.	Removal of many organic and inorganic compounds Treats organic wastes (with high boiling points, low solubility, and polarity), chlorinated hydrocarbons and aromatics Captures volatile organics in gas mixtures	Cost as a function of the frequency of carbon regeneration Contaminant concentrations should be less than 10,000 ppm Suspended solids less than 50 ppm Dissolved inorganics and oil and grease less than 10 ppm

Applicable Treatment Technologies for Wastewater Reuse

Treatment technology	Description	Applications	Limitations
Sedimentation	Sedimentation is a settling process that allows heavier solids to separate from a solution by gravity.	Removal of solids that are more dense than water	Not suitable for wastewaters consisting of emulsified oils
Filtration	Filtration separates and removes suspended solids from a solution by passing the solution through a porous medium (e.g., fabric screen, granular material).	Dewatering sludges and slurries Removal of suspended solids from liquids Pretreatment to remove solids to prevent clogging of subsequent treatment devices (e.g., ion exchange, reverse osmosis, carbon absorption)	Not suitable for reducing toxicity of the wastewater Not suitable for gelatinous solids Limitations on suspended solids concentration of liquids
Evaporation	Evaporation is a physical separation process in which energy is applied to volatilize a solution thereby separating a liquid from dissolved or suspended solids.	Treatment of hazardous wastes Treatment of solvent wastes with nonvolatile constituents (e.g., oil, grease, polymeric resins, paint solids) Separation of dissolved and suspended solids	Effectiveness depends on the volatility of the solution Cost
Dewatering	Dewatering includes any of a number of physical processes (e.g., vacuum filtration, sludge drying belt filter press) used to reduce the moisture content of sludges.	Reducing the moisture content of sludges	Limitations depend on the dewatering process used for a particular type of sludge

Acid and Alkaline Bath Extension

Introduction

The information contained in this report was obtained from:

North Carolina Department of Environment,
Health and Natural Resources
Office of Waste Reduction
P. O. Box 29569
Raleigh, NC 27626-9569

and

Amplate Incorporated
7820 Tyner Street
Charlotte, NC 28262
704/597-0688
(Linda McNabb)

Amplate Incorporated is a company heavily involved in electroplating. This process requires the use of both acid and alkaline baths. The company has found a way to extend the life of the baths and the general summary below describes that bath extension process.

Alkaline Bath Extension

The bath life is extended by in-tank filtration through a 10-35 micron filter in order to remove particulates. The effect of the filtration has extended bath life from three to eighteen months before waste treatment is required.

Acid Bath Extension

The life of the acid bath is extended by first adding a coagulant followed by in-tank filtration. This is the same process that is described above in Alkaline Bath Extension. The coagulant used by Amplate is called **Metal Away**. It is an aqueous solution that is effective in precipitating low concentrations of precious and heavy metal ions from effluent containing 10-500 ppm total metal ions. It is also effective for precipitating much higher levels of metal ions. **Metal Away** is used to precipitate copper, cadmium, iron, magnesium, mercury, nickel, silver, and zinc. **Metal Away** is not recommended for aluminum, arsenic, chromium, and molybdenum. Generally, application requires 2 to 15 parts of coagulant per part of most metal ions. Once the **Metal Away** has precipitated out the heavy metal ions (no pH adjustment is required), these ions are easily removed by almost any standard filtration method. By treating the baths every six to eight weeks, the bath life is extended by at least two years. Amplate has also reused their hydrochloric and nitric acids for almost three years.

Amplate is now able to offer this product as a distributor for those interested in prolonging the life of most acid baths, reducing caustic and acid purchases, and reducing hazardous and nonhazardous waste volumes.

More information on **Metal Away** is available upon request from Amplate Incorporated (see address, phone number, and contact on page 1). A video highlighting this technology is available through Terry Albrecht (919/715-6498) at the North Carolina Department of Environment, Health, and Natural Resources.